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Index at acceptance:—Classes 2(3), C2(A3:A14:R18); and 2(5), R27K6(D:E:F).

International Classification:—C07d. C08g.

COMPLETE SPECIFICATION

Process for the production of Basic N,N'-Diepoxides

We, **FARBENFABRIKEN BAYER AKTIEN-GESELLSCHAFT.** of **Leverkusen-Bayerwerk,** phenyl) methane is mentioned in the specification as being a suitable secondary amino bi-

SPECIFICATION NO. 816,923

The inventors of this invention in the sense of being the actual devisers thereof within the meaning of Section 16 of the Patents Act, 1949, are Gunter Frank, of 25 Kaiserstrasse, Leverkusen, Germany, Richard Wegler, of 2 Auf dem Forst, Leverkusen, Germany, and Walter Krauss, of 3 Hahnenweg, Köln-Stammheim, Germany, all German citizens.

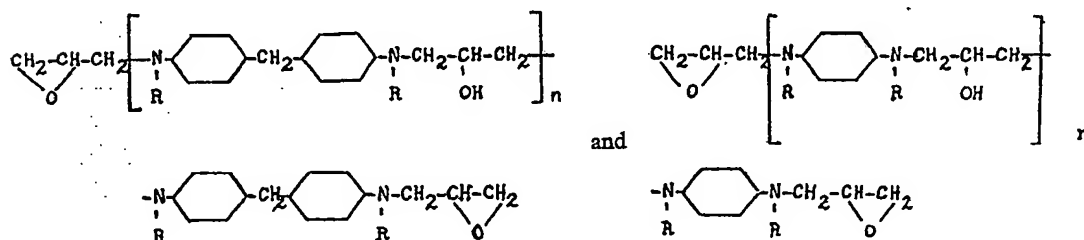
THE PATENT OFFICE,
15th September, 1950

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25 its functional groups being a secondary amine group and the other functional group being either a secondary amine group or a hydroxyl group, is reacted with two mols of epichlorohydrin and its equivalent of alkali to form a compound which is stated in the specification
30 to be a diepoxide. Bis-4,4-(N-methylamino-

4,4'-di-(mono-alkylamino) derivative of a 55
diphenyl methane.

The basic N,N'-diepoxides produced by the process of the present invention have the general formulae



in which each R represents an alkyl radical and in which n is zero or a whole number. It is also possible for one or both methane

hydrogen atoms of any of the diphenyl methane groups to be replaced by an alkyl radical or by a cycloalkyl radical. The length of the chain



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COMPLETE SPECIFICATION

Process for the production of Basic N,N'-Diepoxides

WE, FARBENFABRIKEN BAYER AKTIEN-GESELLSCHAFT, of Leverkusen-Bayerwerk, Germany, a Body corporate, organised under the laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the
10 production of basic N,N'-diepoxides.

It is known that by reacting diphenols, for example 4,4'-dihydroxy-diphenyl-dimethylmethane, with epichlorohydrin in the presence of an alkali metal hydroxide, it is possible to obtain epoxides which can be further processed to form synthetic resins (cf. for example United Kingdom Patent Specification No. 518,057).

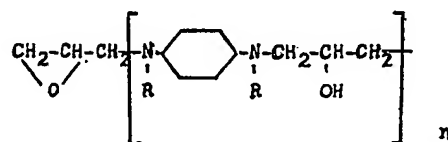
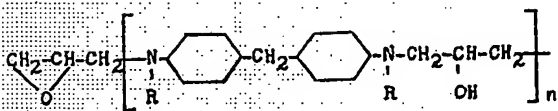
In United Kingdom Patent Specification No. 664,271 there is described a reaction in which one mol of a bifunctional compound having its two functional groups separated by a chain of at least four carbon atoms, one of its functional groups being a secondary amine group and the other functional group being either a secondary amine group or a hydroxyl group, is reacted with two mols of epichlorohydrin and its equivalent of alkali to form a compound which is stated in the specification to be a diepoxide. Bis-4,4-(N-methylamino-

phenyl) methane is mentioned in the specification as being a suitable secondary amino bifunctional compound.

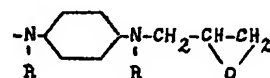
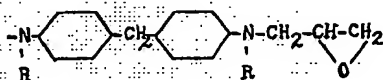
According to the present invention there is now provided a process for the production of basic diepoxides which have terminal nitrogen atoms each carrying one epoxy propane group, which comprises reacting a secondary 4,4'-di-(monoalkylamino) derivative of a diphenyl methane, or a secondary 4,4'-di-(mono-cycloalkylamino) derivative of a diphenyl methane, with more than 1 mol of epichlorhydrin or of a glycerine dichlorhydrin per mol of the derivative of a diphenyl methane, and converting the resulting di-(hydroxy-chloropropyl)-amine into the basic diepoxide by the action of an aqueous solution of an alkali, for example an aqueous solution of a caustic alkali or an aqueous solution of an alkaline reacting compound, at a temperature not exceeding 30° C.

In a modification of the process of the present invention a secondary 1,4-di-(mono-alkylamino) or 1,4-di-(mono-cyclo-alkylamino) derivative of benzene is used in place of the 4,4'-di-(mono-alkylamino) derivative of a diphenyl methane.

The basic N,N'-diepoxides produced by the process of the present invention have the general formulae



and



in which each R represents an alkyl radical and in which n is zero or a whole number. It is also possible for one or both methane

hydrogen atoms of any of the diphenyl methane groups to be replaced by an alkyl radical or by a cycloalkyl radical. The length of the chain

of the basic diepoxides formed depends upon the proportion of the chlorhydrin which is used. The secondary aromatic diamines used as starting material can be produced in known manner by condensation of an N-alkyl- or N-cyclo-alkyl aniline with an aldehyde or ketone, for example formaldehyde or acetone.

It is preferable in some cases for the epoxides to be produced in the presence of an inert solvent, such as benzene or toluene. The addition of a solvent is particularly advantageous if less than 1 mol of epichlorhydrin or glycerine dichlorhydrin is reacted with each secondary amino group, i.e. under conditions which lead to substances which are of comparatively high molecular weight and are consequently solid resinous substances.

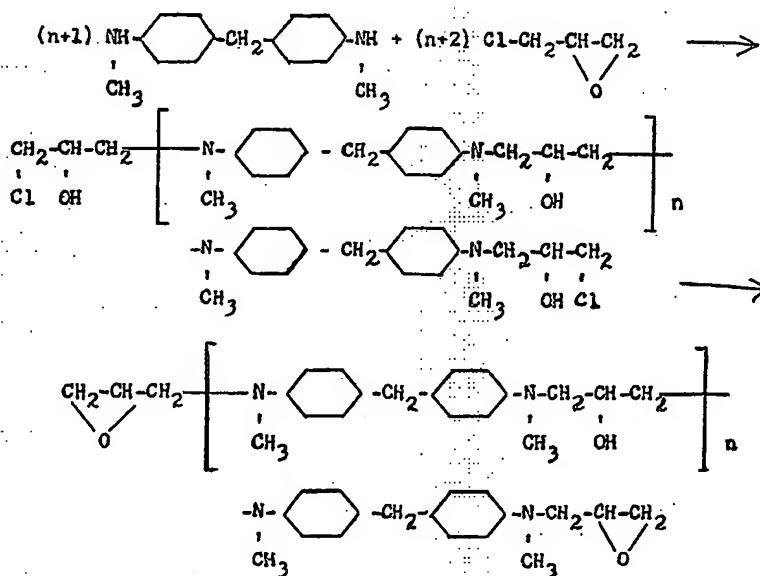
N-methyl aniline is particularly suitable for the production of the secondary amines which are used in the process of the invention. However, it is also possible to use N-alkyl or N-cyclo-alkyl-substituted anilines such as N-ethyl, N-propyl, N-butyl and N-cyclohexyl-anilines.

The condensation with the aldehyde or ketone gives compounds in which two alkyl-aniline radicals are always linked to one another through an unsubstituted methylene group or a mono- or di-substituted methylene group.

The process of the invention can, for example, be carried out by heating the secondary diamine in a solvent, such as benzene, and then adding epichlorhydrin dropwise.

In order to complete the reaction, the reaction mixture is preferably stirred for a time. The hydrogen chloride is then advantageously split off at room temperature by adding the aqueous solution of an alkali. The diepoxide resin thereby formed is recovered from the benzene layer in the usual way. Whether diepoxides of low or high molecular weight are obtained depends on the molar ratio selected between the diamine and epichlorhydrin.

The reaction is illustrated by the following reaction diagram, in which n is zero or a whole number:



The basic diepoxides obtained by the process of the invention can be used for example for the production of plastics, since they can be hardened with all hardening agents known for non-basic diepoxides, such as divalent and polyvalent alcohols, carboxylic acids, amines, amides (carboxylic acid amides or sulphonic acid amides), melamine resins, urea resins or phenolic resins. It is also possible to work in the presence of diluents, if this should be desired, and it is also possible to use such diluents as participate in the reaction, for example phenoxypropane oxide glycidic ethers or basic propane oxides.

The basic diepoxides obtained by the process of the invention offer particular advantages

when they are hardened with polybasic aliphatic amines, since the low viscosity of the reaction mixture enables sheets to be cast free from bubbles, and since the plastics formed by this hardening have properties which are superior in many respects to those of plastics which have been manufactured using diphenols. The mechanical properties are more favourable in many respects, and also the electrical properties show a substantial improvement.

The basic diepoxides obtained by the process of the invention behave in a particularly advantageous manner towards cyclic dicarboxylic acid anhydrides, and a substantially more rapid hardening is obtained than when

non-basic diepoxides are used. This renders possible the production of cold-hardening coatings or bonding layers and also laminated masses.

5 Moreover, substantial advantages are obtained when novolaks which are not self-hardening are used for the hardening process.

Whereas non-basic diepoxides react only to a comparatively small extent with novolaks, or only after the addition of a catalyst with a strongly alkaline action, basic diepoxides when heated produce satisfactory hardening even without a catalyst, owing to their natural basic nature. If it is desired further to accelerate the reaction, it is possible to add more strongly basic mono- or diepoxides, which can be obtained, for example, from aliphatic primary or secondary amines. A relatively large addition of monoepoxide compounds causes the formation of predominantly linear addition products which are not cross-linked.

It was surprising that the basic aromatic N,N'-diepoxides could be obtained on a technical scale in such excellent yields (95—98%), since it is known that the basic aromatic monoepoxides are obtained only in a yield of approximately 70—75% (Journal Chemical Society 1950, 893). The basic diepoxides which are obtainable by the process of the invention

can also be hardened in admixture with any desired other diepoxides.

The following examples further illustrate the invention.

EXAMPLE 1.

1582 Gram (=7 mols) of 4,4'-di-(mono-methylamino)-diphenyl methane are dissolved in 1.4 litres of benzene. The mixture is boiled and 1400 grams of epichlorhydrin are added dropwise at the boiling point over a period of 2—2½ hours while stirring. The mixture is heated for a further 15 hours while stirring, cooled to 20° C., and 2.1 litres of 44% sodium hydroxide solution are added dropwise over a period of 2 hours. The temperature is not allowed to exceed 30° C. After addition of the sodium hydroxide solution the mixture is stirred vigorously for 15 hours at room temperature and such an amount of water is added that the precipitated sodium chloride just redissolves (1.5 litres); the resulting mixture is allowed to settle, and the layers formed are separated. The benzene solution is briefly dried with solid potassium hydroxide and the benzene is distilled off. The last traces of solvent are removed under high vacuum. A resin is obtained which is still liquid and light brown in colour. Yield: 2322 grams=98% of the theoretical.

Analysis for $C_{21}H_{26}O_2N_2$

Calculated: C 74.55% H 7.69% N 8.28% O 9.46%

Found: C 74.40% H 7.91% N 8.00% O 9.40%

EXAMPLE 2.

226 Grams (=1 mol) of 4,4'-di-(mono-methylamino)-diphenyl methane are dissolved in 300 cc. of benzene and heated to boiling point. 139 Grams of epichlorhydrin (=1.5 mol) are added dropwise over a period of 15 minutes, and the mixture is heated for a further 15 hours and cooled to 20° C. 225 Cc. of 44% sodium hydroxide solution are added dropwise over a period of about 30 minutes, stirring is then continued for 15 hours and finally such an amount of water is added that the precipitated sodium chloride redissolves (100 cc.). The layers are separated, the benzene layer is briefly dried with potassium hydroxide, and the benzene is distilled off, leaving a light-coloured clear resin. Yield: 372 grams=87% of the theoretical; softening point: 33—36° C.

Analysis for $C_{39}H_{48}O_3N_4$

Calculated: C 75.48% H 7.74% O 7.74% N 9.03%

Found: C 75.15% H 7.87% O 7.60% N 9.35%

EXAMPLE 3.

226 Grams (=1 mol) of 4,4'-di-(mono-methylamino)-diphenyl-methane are heated to boiling point in 200 cc. of benzene. 111 Grams (=1.2 mol) of epichlorhydrin are added over a period of 15 minutes and the mixture is stirred for 15 hours. It is then cooled to 20° C., another 200 cc. of benzene are added, and 180 cc. of 44% sodium hydroxide solution are introduced dropwise over a period of 15 minutes. The mixture is stirred for 15 hours at room temperature. 100 cc. of water are added and the layers are separated. The benzene solution is briefly dried with caustic potash and the benzene is distilled off, leaving a clear brown resin. Yield: 270 grams=92% of the theoretical.

Analysis for $C_{93}H_{114}O_8N_{10}$

Calculated: C 76.12% H 7.77% O 6.54% N 9.54%

Found: C 76.30% H 7.95% O 6.61% N 9.28%

EXAMPLE 4.

762 Grams (3 mols) of 4,4'-di-(mono-ethyl-amino)-diphenyl methane are dissolved in 600 cc. of benzene and heated to boiling point. 600 Grams of epichlorhydrin are added dropwise and the mixture heated for about 15 hours under reflux. The resulting mixture is then cooled to 20—25° C. and 900 cc. of 40% sodium hydroxide solution are added dropwise.

Stirring is continued for 15 hours, 600 cc. of water are admixed, and the benzene layer is isolated and is filtered in the presence of carbon. The solvent is distilled off, finally under high vacuum, with a bath temperature of 100° C. 1002 Grams = 91% of a brown liquid resin are left.

Molecular weight: found 425, calculated 366.

Analysis: for $C_{23}H_{30}O_2N_2$

Calculated: C 73.40% H 8.19% O 8.74% N 7.65%
C 75.20% H 8.10% O 8.64% N 7.60%

EXAMPLE 5.

136 Grams ($\frac{1}{2}$ mol) of 1,4-di-(mono-cyclo-hexylamino)-benzene are dissolved in 200 cc. of methanol and heated to boiling point. While the solution is boiling, 100 grams of epichlorhydrin are added dropwise, the solution is heated for 5 hours under reflux, the alcohol is distilled off, 200 cc. of benzene are added and

130 cc. of 40% sodium hydroxide solution are introduced dropwise at 20—25° C. The mixture is stirred for a further 12 hours, 100 cc. of water are added, and the benzene layer is isolated. After filtration of this layer through carbon, the solvent is distilled off, and there remain 159 grams = 83% of the theoretical of a brown resin.

Analysis for $C_{24}H_{36}O_2N_2$

Calculated: C 75.00% H 9.37% O 8.33% N 7.29%
Found: C 74.82% H 7.1% O 8.03% N 7.2%

WHAT WE CLAIM IS:—

1. A process for the production of basic diepoxides which have terminal nitrogen atoms each carrying one epoxy propane group, which comprises reacting a secondary 4,4'-di-(mono-alkylamino) derivative of a diphenyl methane, or a secondary 4,4'-di-(mono-cyclo-alkylamino) derivative of a diphenyl methane, with more than 1 mol of epichlorhydrin or of a glycerine dichlorhydrin per mol of the derivative of a diphenyl methane, and converting the resulting di-(hydroxy-chloropropyl)-amine into the basic diepoxide by the action of an aqueous solution of an alkali at a temperature not exceeding 30° C.

2. A process as claimed in claim 1, wherein 4,4'-di-(mono-methylamino) diphenyl methane is reacted with more than 1 mol of epichlorhydrin per mol of the (mono-methylamino) diphenyl methane, and the reaction product formed is converted into the basic epoxide by the action of an aqueous solution of an alkali at a temperature not exceeding 30° C.

3. A process as claimed in claim 1 or 2, wherein the reaction with the chlorhydrin is carried out in the presence of a solvent.

4. A modification of the process claimed in claim 1, wherein a secondary 1,4-di-(mono-alkylamino) or 1,4-di-(mono-cyclo-alkylamino) derivative of benzene is used in place of the

4,4'-di-(mono-alkylamino) derivative of a diphenyl methane.

5. A process as claimed in claim 4, wherein the reaction with the chlorhydrin is carried out in the presence of a solvent.

6. A process for the production of basic epoxides which have terminal nitrogen atoms each carrying one epoxy propane group, substantially as described with reference to any of Examples 1—4.

7. A process for the production of basic epoxides which have terminal nitrogen atoms each carrying one epoxy propane group, substantially as described with reference to Example 5.

8. Basic epoxides which have terminal nitrogen atoms each carrying one epoxy propane group, whenever produced by the process claimed in claim 1, 2, 3 or 6.

9. Basic epoxides which have terminal nitrogen atoms each carrying one epoxy propane group, whenever produced by the process claimed in claim 4, 5 or 7.

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